

Report of the experiment 08-01-854: EXAFS experiment to investigate the effect of the Ag site on the refractive index of Ag-doped glass waveguides.

The aim of the experiment was to investigate the effect of the Ag site on the refractive index of Ag-for-Na ion-exchanged glass waveguides.

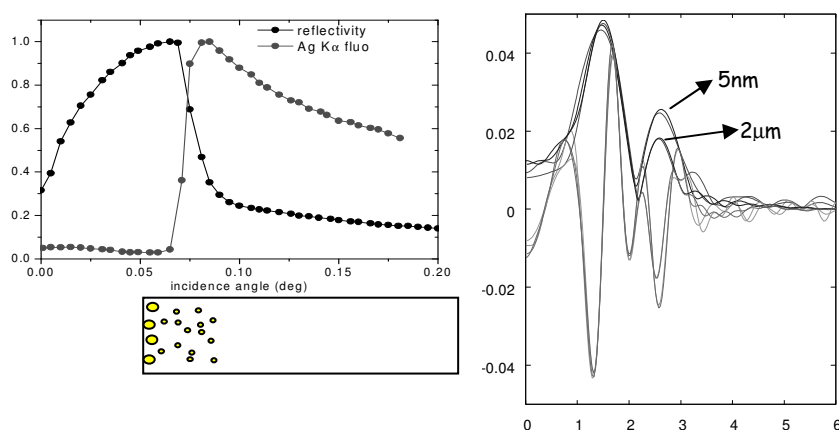
An EXAFS + reflEXAFS experiment at the Ag K-edge allowed investigating the Ag site in Ag-for-Na ion-exchanged glass waveguides.

We have measured ion-exchanged waveguides doped with Ag at different concentration (average Ag/Na ratio = 0.1-0.8). The most interesting results are obtained in grazing incidence geometry, with the incidence angle very close to the critical one. This geometry required a high stability of both the x-ray beam and of the sample holder (the critical angle is about 0.08 deg), see figure (left panel). The incidence angle was chosen to probe different thickness, from  $\approx 5$  nm to few  $\mu\text{m}$ .

A collection of 5 different samples were measured at different incidence angle, at room temperature and in fluorescence mode (a 13-elements HP Ge detector was used).

We obtained an unexpected result since, apart from the usual Ag-O coordination, already investigated in a previous experiment (see the corresponding paper: C. Maurizio et al., *J. Phys. Chem. C* **113** (2009) 8930) and visible in the EXAFS signal of all the samples, a Ag-Ag coordination is also well visible in the Fourier transform moduli of the EXAFS spectra when the probed depth is less than few  $\mu\text{m}$ .

Actually, the ReflEXAFS measurements pointed out that the surface layer present a significant contribution from metallic Ag, even if the glass underwent an ultrasound bath of  $\text{FeNO}_3$  water solution to dissolve the metallic Ag. The metallic fraction decreases as the probed thickness is increased (See the pseudo-radial distribution function of atoms around the Ag site from EXAFS in the figure, right panel). The Ag clusters (small, likely below 1 nm, since the Ag-Ag distance is  $\approx 2.7$ , to be compared with the value of 2.88 for the Ag bulk) are likely located in a sub-surface layer; moreover, the variation of the Ag-Ag distance as a function of the penetration depth suggests that larger clusters are located closer to the surface. The picture that comes out from the EXAFS data is schematically represented in figure (bottom-left panel).



Further analysis are in progress to better quantify i) the cluster size, ii) the metallic fraction at different depths, iii) the Ag-O coordination at different depths. These results will be related with the refractive index variation induced by the Ag ions.